Now You See It—Now You Don't

An Oscillating Chemical Reaction

Introduction

Surprise your students with this demonstration of an oscillating chemical reaction that changes color in a rhythmic fashion. Addition of three white solids to a colorless solution results in a color change to orange. In less than one minute, the solution reverts back to its original colorless state. The color of the solution continues to oscillate every 30 seconds between colorless and orange for another 30 minutes. Abstract principles—the nature of a reaction mechanism and the existence of intermediates along a reaction pathway—come to life in this engaging demonstration.

Concepts

- Oscillating chemical reaction
- Catalyst
- Oxidation–reduction reaction

Materials

Malonic acid, $CH_2(CO_2H)_2$, 4.5 g

Manganous sulfate, $MnSO_4{\cdot}H_2O$, 1.3 g

Potassium bromate, $KBrO_3$, 4.0 g

Sulfuric acid solution, H_2SO_4, 1.5 *M*, 400 mL

Beaker, 1-L

Graduated cylinder, 500-mL

Magnetic stirrer and magnetic stir bar

Plastic weighing dishes, 3

Safety Precautions

Sulfuric acid solution is severely corrosive to eyes, skin, and other tissue. Malonic acid is a strong irritant and is slightly toxic. When dissolved in water it is a strong acid that is corrosive to eyes, skin, and the respiratory tract. Potassium bromate is an oxidizer and presents a fire risk in contact with organic materials. It is a strong irritant and moderately toxic. This reaction generates a small amount of elemental bromine in aqueous solution. Bromine water is toxic by inhalation and ingestion and is a skin irritant. Provide adequate ventilation. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Please review current Material Safety Data Sheets for additional safety, handling, and disposal information.

Preparation

The following preparation steps may be completed before the demonstration. Measure or weigh out the required amounts of each of the following reagents: 400 mL of 1.5 *M* sulfuric acid solution in a 500-mL graduated cylinder, and 4.5 g of malonic acid, 4.0 g of potassium bromate, and 1.3 g of manganous sulfate in separate, labeled weighing dishes or small beakers.

Procedure

1. Transfer 400 mL of 1.5 *M* sulfuric acid solution to a 1-L beaker containing a magnetic stirring bar.
2. Place the beaker on a magnetic stirrer and adjust the speed of the stirrer to ensure thorough and continuous mixing of the solution.
3. Transfer 4.5 g of malonic acid to the beaker and stir until it is completely dissolved.
4. Add 4.0 g of potassium bromate to the resulting colorless solution and stir until dissolved.
5. Transfer 1.3 g of manganous sulfate to the beaker and continue stirring. Observe the solution as it turns amber-orange in color.
6. Within about 90 seconds the solution will revert to its original colorless state. This cycle will repeat itself approximately every 30 seconds for up to 30 minutes. The period between color oscillations will gradually increase as the reaction continues.

Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures governing the disposal of laboratory waste. The reaction mixture can be neutralized with sodium carbonate and flushed down the drain with excess water according to Flinn Suggested Disposal Method #24a.

Connecting to the National Standards

This laboratory activity relates to the following National Science Education Standards (1996):

Unifying Concepts and Processes: Grades K–12
Constancy, change, and measurement
Content Standards: Grades 9–12
Content Standard B: Physical Science, structure and properties of matter

Tips

- The equipment and glassware used in this demonstration should be clean and free of chloride ion contamination. Rinse all equipment and glassware in distilled water before use. Even small amounts of chloride ion can inhibit the reaction mechanism responsible for the oscillating reaction behavior.
- The use of a magnetic stirrer is highly recommended and will produce the best results. The color change becomes more distinct as the reaction proceeds—the colorless phase may initially have a bit of a rose tint.
- This is the simplest of the oscillating chemical reactions to perform, both in terms of the number of chemicals involved and the relative ease of interpreting the reaction behavior.

Discussion

At first glance, the unusual observations in this demonstration seem to contradict traditional chemical wisdom. Experience suggests that if a chemical system is left undisturbed, reactants should disappear and products should appear in a continuous manner, until equilibrium is reached. Oscillating chemical reactions appear to violate this wisdom, as an intermediate product (color) appears, disappears, and then reappears in a cycle that repeats itself over and over again. Several factors have been found to be important in setting up conditions for an oscillating chemical reaction to take place. First of all, the reaction conditions (concentrations of reactants) should be far away from their equilibrium values. Secondly, there must be two competing reaction pathways available for the overall reaction to take place. If one of the pathways produces an intermediate, while the other pathway consumes it, then the concentration of that intermediate acts like a trigger and the overall reaction switches back and forth from one pathway to another, like a pendulum.

This oscillating chemical reaction demonstrates a modified Belousov-Zhabotinsky (BZ) reaction, manganese(II) catalyzed oxidation of malonic acid by bromate ion. The overall redox reaction is summarized in Equation 1. Oxidation of malonic acid to carbon dioxide, formic acid, and water is accompanied by reduction of bromate ion to bromide ion. The reaction requires the presence of Mn^{2+} catalyst.

$$CH_2(CO_2H)_2 + BrO_3^- \xrightarrow{Mn^{2+}} HCO_2H + 2CO_2 + H_2O + Br^- \qquad \textit{Equation 1}$$

The balanced chemical equation does not provide any insight into how the reaction actually takes place. All of the reagents are colorless and cannot be responsible for the orange color observed. In order to understand the observations it is nesessary to recall the idea of a catalyst and to propose the existence of at least one orange-colored chemical intermediate.

Since Mn^{2+} is required for the reaction to start, but is neither a reactant nor a product, it must be acting as a catalyst. Assume that the catalyst allows the reaction to occur via a pathway that involves the formation and subsequent reaction of at least one chemical intermediate. This assumption explains two key observations: (1) the role of manganese ion in jump-starting the reaction, and (2) the appearance followed by disappearance of the orange color. The orange color is not associated with any of the reactants or products, and so it must arise from a chemical intermediate. The characteristic orange color of bromine is well-known. Bromine may be the missing chemical intermediate!

The key to understanding the repeated appearance and disappearance of bromine is a second assumption: there are actually two competing reaction pathways for reduction of bromate ion. The observed oscillation reflects which pathway prevails under different conditions. The two competing pathways are fundamentally different. In Process A, electrons are exchanged one electron at a time and Mn^{2+} reduces bromate to bromine (Equation A1) and is itself converted to Mn^{3+}. The bromine is able to react with malonic acid via Equation B2, and bromide is formed as an overall product. In Process B, however, bromide ion appears as a reactant, transferring electrons two at a time (like Noah's Ark!) and reducing bromate ion to bromine (Equation B1). The limiting factor that determines whether Process A or Process B predominates is the bromide ion concentration. Bromide ion is not only a product of the overall reaction, as noted in Equation 1, but also a reactant in Process B.

The demonstration begins with Process A. Process B takes over when the concentration of bromide ion, formed as a product in reaction A2, rises above a critical level. As Process B continues, it depletes the bromide ion concentration—conditions that favor Process A once again. The reaction switches between Process A and Process B, triggered by changes in the bromide ion concentration. The concentrations of other species in solution oscillate as well; these concentration changes explain the observed rhythmic color change.

Process A

$$2BrO_3^- + 12H^+ + 10Mn^{2+} \rightarrow Br_2 + 10Mn^{3+} + 6H_2O \qquad \textit{Equation A1}$$

Bromate ions are reduced by manganese(II) ions to produce bromine through a simple redox reaction as shown in *Equation A1*. Process A produces Mn(III) ions and Br_2. Both of these species react at least in part to oxidize the malonic acid (see *Equation B2*) and the bromomalonic acid (see *Equation A2)* to form bromide ions. As the concentration of bromide ions increases, the rate of *Equation B1* increases until Process B begins to dominate.

$$BrCH(CO_2H)_2 + 4Mn^{3+} + 2H_2O \rightarrow Br^- + 4Mn^{2+} + HCO_2H + 2CO_2 + 5H^+ \qquad \textit{Equation A2}$$

Process B

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \qquad \textit{Equation B1}$$

Bromate is reduced by bromide ions through a series of oxygen transfers (two-electron reductions) as shown in *Equation B1*. The orange color which develops is caused by the production of elemental bromine. The color soon disappears as the bromine reacts with malonic acid as shown in *Equation B2*.

$$Br_2 + CH_2(CO_2H)_2 \rightarrow BrCH(CO_2H)_2 + Br^- + H^+ \qquad \textit{Equation B2}$$

Process B results in an overall decline in the bromide ion concentration and, once the necessary intermediates are generated and most of the bromide ions are consumed, the rate becomes negligible and Process A again takes over.

Reference

Shakhashiri, B. Z., *Chemical Demonstrations: A Handbook for Teachers of Chemistry;* University of Wisconsin Press: Madison 1985; Vol. 2, pp 257–261.

Now You See It—Now You Don't—An Oscillating Chemical Reaction is available as a Chemical Demonstration Kit from Flinn Scientific, Inc.

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